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(54) Name of the invention: Capsulated Type Recurrent Reflctive Sheeting

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[ Note : Names, addresses, Company names and brand names are translated in the most common manner. Japanese Language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note.]

(54) [Name of the invention]

Capsulated type recurrent reflective sheeting

(57) [ Summary]

[Goal]

The goal of the present invention is to suggest a capsulated type recurrent reflective sheeting, with excellent properties, by using advantageously a substrate material film with capsule wall forming properties, where the formed capsule wall has excellent thermal melting shape change properties, and adhesive strength onto the protective film, it has excellent deformation resistant properties, elongation strength resistance to repeated contraction properties, and also this film has outdoor long term resistance weather properties.

[Structure]

A recurrent reflective sheeting, characterized by the fact that it is capsulated type recurrent refractive sheeting that is formed from at least a transparent to the light protective film, a supporting film and a continuous wall that is formed by thermal melting shape change from the above described supporting film; where the gap that remains in the space between the above described protective film and the supporting film is partially connected by the above described continuous wall, and recurrent reflection elements are densely positioned along the whole surface of the above described protective film and /or the supporting film; and in this recurrent reflection sheeting type, the above described supporting film contains a matrix resin and a fiber type material.

[Range of the claims of the present invention]

[Claim 1]

A recurrent reflective sheeting, characterized by the fact that it is capsulated type recurrent refractive sheeting that is formed from at least a transparent to the light protective film, a supporting film and a continuous wall that is formed by thermal melting shape change from the above described supporting film; where the gap that remains in the space between the above described protective film and the supporting film is partially connected by the above described continuous wall, and recurrent reflection elements are densely positioned along the whole surface of the above described protective film and /or the supporting film; and in this recurrent reflection sheeting type, the above described supporting film contains a matrix resin and a fiber type material.

[Claim 2]

A capsule type recurrent reflective sheeting according to the above described claim 1 of the present invention, where the fiber type material is contained in an amount in the range of 0.1 ~ 30 weight parts, relative to 100 weight parts of the matrix resin material.

[Claim 3]

A capsule type recurrent reflective sheeting according to the above described claim 1 or claim 2 of the present invention, where the average fiber length of the fiber type material is in the range of 1 ~ 100 microns.

[Claim 4]

A capsule type recurrent reflective sheeting according to the above described claims 1 ~ 3 of the present invention, where the average fiber diameter of the fiber type material is in the range of 0.01 ~ 10 microns.

[Claim 5]

A capsule type recurrent reflective sheeting according to any of the above described claims 1 ~ 4 of the present invention, where the average aspect ratio of the fiber type material is in the range of 2 ~ 5,000.

[Claim 6]

A capsule type recurrent reflective sheeting according to the above described claims 1 ~ 5 of the present invention, where the fiber type material is a whiskers type fiber material.

[Claim 7]

A capsule type recurrent reflective sheeting according to the above described claim 6 of the present invention, where the whisker material is at least one type of whisker material selected from the group of an alkali metal titanate type whisker material, zinc oxide type whisker material and silicon carbide whisker material.

[Claim 8]

A capsule type recurrent reflective sheeting according to the above described claims 1 or 2 of the present invention, where the matrix resin is an acrylic type resin that has a glass transition point temperature that is in the range of -50 ~ 30°C.

[Claim 9]

A capsule type recurrent reflective sheeting according to the above described claim 1 of the present invention, where the elongation strength of the supporting film at 23°C is at least 50 kg/cm<sup>2</sup>, and also, the elongation at break is at least 50 %.

[Detailed description of the invention]

[0001]

[Technological sphere of application]

The present invention is an invention about a capsule type recurrent reflective sheeting that can be used in road sign applications, industrial signs applications, etc., sign type applications, in automobiles, motorcycles etc., transportation number plates application, clothing, instruments etc., safety materials application, or observation plates etc., marking type applications.

[0002]

[Previous technology]

In the past, a recurrent reflective sheeting that reflects recurrently in the direction of the light source, has been well known. And by using its recurrent reflective properties advantageously, the above sheeting material has been widely and advantageously used in different types of applications such as the above described. Among those sheeting materials the so-called capsule type recurrent reflective sheeting has found increasing applications during the years because of its excellent capabilities for light reflection. And this so-called capsule type recurrent reflective sheeting is formed from at least a transparent to the light protective film, a supporting film and a continuous wall that is formed by thermal melting shape change from the above described

supporting film; where the gap that remains in the space between the above described protective film and the supporting film is partially connected by the above described continuous wall, and air is entrapped and capsules are formed; and on the protective film and /or on the supporting film inside these capsules, lense type recurrent reflection elements, line the cube cone type recurrent reflective type elements are densely positioned.

[0003]

Regarding such capsule type recurrent reflective sheeting material, the magnitude of its recurrent reflection capability is the most important function desired, and in addition to that, even in the case when it is used for severe conditions like outdoor type of applications, the most important capability is the weather resistance properties representing the capability of sustaining these excellent recurrent reflection properties over a prolonged periods of time.

[0004]

The decrease of the recurrent reflective capability of the capsule type recurrent reflective sheeting in the case when the sheeting is used for outdoor applications for prolonged periods of time, almost in all cases is due to the destruction of the capsules, which occurs by the penetration of the rain water etc., inside them. For example, because following the changes in the temperature of the outside air atmosphere, the gas that is inside the capsules is repeatedly expanded and contracted; or the protective film is cracked because of the repeated expansion and contraction of the metal plate etc., that is glued onto the recurrent reflective sheeting material; or the adhesion between the protective film and the continuous wall interface is destroyed; or the continuous wall itself is destroyed or the supporting film itself is destroyed; etc., the gas impermeability properties of the capsules are lost and rain water etc., penetrates into the capsules. And because of that the refractive coefficient conditions in the capsules, which are the most important reason for the recurrent reflection function, are changed, and the enclosed recurrent reflective elements are deteriorated and the light reflective function is lost. And by that the recurrent reflective capability is decreased.

[0005]

Among those, the continuous wall that connects the protective film and the supporting film has the tendency to break most easily because of the adverse effects of the deformations etc., on its structure. And at the time of the practical implementation, there are many cases where the deterioration of the recurrent reflective sheeting and the decrease of the capsule type recurrent reflective properties are due to the destruction of the continuous wall. Consequently, in order to improve the weather resistant properties of the

capsule type recurrent reflective sheeting material, the most important thing is to form a continuous wall with an excellent strength.

[0006]

In the past, there have been several experiments with the goal to increase the strength of the continuous wall in order to improve the weather resistant properties of the capsule type recurrent reflective sheeting material. For example, according to the description disclosed in the Japanese Patent Application Laid-Open Number Showa 62-121043, as the supporting film that forms the continuous wall a high molecular weight thermoplastic resin film is used and by that toughness and elastic properties are imparted onto the supporting film material, and it is suggested that even better structural unity properties are imparted onto the recurrent reflective sheeting material.

[0007]

However, in the case of this suggestion, the increase of the toughness and elastic properties of the supporting film requires a large increase in the molecular weight of the resin material used for the formation of the supporting film. And because of that when by increasing the molecular weight of the resin used for the formation of the supporting film strong hardness properties are obtained in the continuous wall or in the supporting film material itself, generally the thermal melting shape change properties of the supporting film are deteriorated and there is the trend that the adhesive properties between the continuous wall and the protective film, are decreased. On the other hand, if, in order to obtain sufficient thermal melting shape change properties and flexibility properties, the molecular weight of the resin material used for the formation of the supporting film, is decreased, the hardness properties are lost and it is not possible to achieve the initial goal. Then, in the case of the suggested according to the above described patent application, where an aliphatic polyurethane polymer material or ethylene or propylene copolymer materials, etc., are used sufficient weather resistant properties are not obtained and it is not appropriate to use in applications where long term weather resistance properties are used.

[0008]

Also, for example, according to the description reported in the Japanese Patent Number Showa 61-13561, a design is suggested where the continuous wall is formed by the thermal melting shape change of a binder agent material (binder agent composition) and after that a radiation beam is irradiated to that continuous wall and by that the continuous wall is cured and the strength is increased. However, according to this invention, when the continuous wall is cured it becomes hard and brittle and because of that it is difficult to also obtain flexibility properties allowing resistance to repeated expansion and

contractions. And also, there is the problem that the recurrent reflective sheeting material also becomes hard etc.. Then, regarding the curing of the continuous wall by using a radiation beam, there is the drawback point that by the volume shrinkage of the continuous wall large deformations are generated.

[0009]

Then regarding the crosslinking (curing) component that has, for example, an unsaturated bond, and that is used in the radiation cure reaction, it is rare that at the time of the curing reaction the whole amount of that component is reacted. And in many cases, its unreacted component, in the state as it is remains in the supporting film or the continuous wall etc., of the manufactured product of the recurrent reflective sheeting material. And because of that there are the problems that by the effects of the heat and sun light etc., outside influences, at the time of the use of the above described recurrent reflective sheeting material, an undesirable cure reaction continues. By that the adhesive strength between the protective film and the continuous wall is reduced and the supporting film and the continuous wall become brittle and it becomes easy for the capsules to be destroyed.

[0010]

Besides that according to the descriptions in the Japanese Patent Application Laid-Open Number Showa Number 60-19445 and the Japanese Patent Application Laid-Open Number Hei-Sei 2-196653, the described here below experiments have been suggested in order to resolve the above described problems. Namely, the structure of the supporting film is made of two layers, the surface layer (binder layer, upper layer side) and a reinforcing layer (support layer, bottom layer side). And by using crosslinking agents like isocyanate etc., in the reinforcing layer, a crosslinked resin layer is obtained and elastic strength is imparted onto the supporting film that it is used in. And to that a surface layer is combined that is formed by using a non-crosslinked resin material or crosslinked resin material, that is crosslinked by using the same crosslinking agent as that used in the reinforcing layer.

[0011]

According to this suggestion, it is possible to design the increase of the elastic strength of the supporting film by using the reinforcing layer and to a certain extent it is also a material where the weather resistant properties are improved. However, the surface layer is formed from the above described crosslinked resin material and it is difficult to select the timing of the formation of the continuous wall by the thermal melting shape change of the crosslinking agent containing surface layer. And also, there is the generation of the same problems that are described here above, in the case according to



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the suggested in the Japanese Patent Number Showa 61-13561. On the other hand, if the surface layer is formed from a resin material not containing a crosslinking agent, the same problems are generated as it has been described in the case of the material suggested according to the Japanese Patent Application Laid-Open Number Showa 62-121043, etc.. And it is still difficult to obtain a material with sufficient properties.

[0012]

**[Problems solved by the present invention]**

The goal of the present invention is to suggest a capsule type recurrent reflective sheeting where the shape can be easily thermally changed and it has excellent thermal melting shape change properties and at the time of the thermal melting shape change for the formation of the continuous wall, it is possible maintain excellent adhesive strength properties in the space between the protective film and the continuous wall, and then, there is little deformation of the supporting film that is forming the capsule walls and of the continuous wall. And by the invention of a supporting film that has excellent elongation strength and excellent flexibility properties that provide resistance to repeated elongations and contractions, and not only that, but also, it has excellent long term outdoor weather resistance properties, the above described problems incurred by using the previous technologies, have been resolved. And by that a capsule type recurrent reflective sheeting with excellent properties is suggested.

[0013]

The authors of the present invention have conducted different experiments regarding the capsule type recurrent reflective sheeting material. As a result from these experiments they have observed that if the supporting film is formed from a matrix resin containing whiskers (fiber shaped metal compound monocrystals) etc., fibrous material, the above described problems according to the previous technology are solved. By that the present invention has been achieved.

[0014]

**[Measures in order to solve the problems]**

According to this invention, a recurrent reflective sheeting is suggested that is characterized by the fact that it is capsulated type recurrent refractive sheeting that is formed from at least a transparent to the light protective film, a supporting film and a continuous wall that is formed by thermal melting shape change from the above described supporting film; where the gap that remains in the space between the above described protective film and the

supporting film is partially connected by the above described continuous wall, and recurrent reflection elements are densely positioned along the whole surface of the above described protective film and /or the supporting film; and in this recurrent reflection sheeting type, the above described supporting film contains a matrix resin and a fiber type material.

[0015]

Here below, the capsulated type recurrent refractive sheeting material according to the present invention will be explained in more details.

[0016]

The capsulated type recurrent refractive sheeting material according to the present invention has as its most important characteristic the fact that the supporting film has a structure that is formed from a matrix resin containing a fibrous type of material.

[0017]

Regarding the above described fibrous type material, it is considered that it functions as an improvement agent for the supporting film material, and it is a material that does not deteriorate the thermal melting shape change properties of the above described supporting film material, and it imparts the functions of excellent repeated elongation - contraction resistance strength, thermal resistance properties, impact resistant strength, high elastic properties, high toughness to break properties, dimensional stability properties etc., functions. And as a result from that it is assumed that it is a material that imparts weather resistance etc., properties onto the capsulated type recurrent refractive sheeting material according to the present invention.

[0018]

Regarding the amount of the fibrous material that is contained inside the supporting film material according to the present invention, relative to 100 weight parts of the matrix resin that forms the structure of the above described supporting film material, it is preferred to be in the range of 0.1 ~ 30 weight parts, more preferably, in the range of 0.5 ~ 20 weight parts, and especially preferably, it is in the range of 1 ~ 15 weight parts. In the case when the amount of the contained fibrous material is higher than the lower limit, it is a preferred option because sufficient impact resistance strength, thermal resistance properties etc., are obtained. Also, if the above described contained amount is less than the above described upper limit, it is preferred because there is no generation of troubles like a deterioration of the thermal melting shape change properties, and lack of sufficient adhesive strength properties in the space between the protective film and the continuous wall.

[0019]

There are no specific limitations regarding the shape of the used fibrous type material, and it is possible to use fibrous type materials with a needle type shape, or a tetrapot type shape etc.. However, if materials are used where the fiber length is significantly large or materials where the fiber diameter is significantly large, there is the trend that the thermal melting shape change properties are deteriorated. And also, if materials are used where the fiber length is significantly large or materials where the fiber length is significantly small, there is the trend that it is difficult for an improvement effect to be observed in the supporting film material. And because of that it is preferred and appropriate to use materials where the average fiber length is in the range of 1 ~ 100 microns, and more preferably, materials where it is in the range of 1 ~ 70 microns, and then still more preferably, materials where the fiber length is in the range of 2 ~ 50 microns. However, it is also preferred to use materials where the fiber diameter is in the range of 0.01 ~ 10 microns, and more preferably, it is in the range of 0.05 ~ 5 microns, and then more preferably, it is in the range of 0.1 ~ 3 microns. Also, regarding the aspect ratio of the above described fibrous material, it is preferred to use materials where it is in the range of 2 ~ 5000, more preferably, in the range of 3 ~ 1000, and then still more preferably a material where the aspect ratio is in the range of 5 ~ 800, and especially most preferably it is in the range of 10 ~ 500.

[0020]

Also, there are no particular limitations regarding the type of the fibrous material that is used. For example, pulp or cotton, wood etc., natural cellulose fibers; silk, wool etc., natural protein fibers, for example, viscous Rayon, acetate Rayon, Benberg Rayon, polyester fiber, polyamide fiber, acrylic fiber, polypropylene fiber etc., synthetic or semi-synthetic fiber; for example, glass fiber, carbon fiber, asbestos fiber, whiskers etc., inorganic material fibers; etc., can be used. Regarding these fibrous type materials, depending on the requirements, they are cut, pulverized or ground, and preferably, it is a good option if after that the obtained material has an average fiber length, average diameter and aspect ratio, that are within the above described limits. Also, regarding these fibrous type materials, each of them correspondingly can be used individually or in a combination of 2 and more types. Among those fibrous type materials, from the point of view of the demonstration of the improvement effect, the whiskers are preferably used.

[0021]

Regarding the above described whiskers, they are metal compounds with a fiber shape particles with a good monocrystallinity. For example, sapphire type, berilium type, boron carbide type, boron silicon type, silicon nitride type,

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zinc oxide type, alkali metal titanates etc., can be used. And among them, it is especially preferred and appropriate to use the relatively inexpensive and also possessing excellent shape homogeneity, silicon carbide type materials, zinc oxide type materials and alkali metal titanate type materials.

[0022]

Regarding matrix resin that forms the structure of the supporting film material in the capsulated type recurrent refractive sheeting material according to the present invention, it is limited to materials that show thermal melting flowability properties at the time of the formation of the continuous wall by using a thermal melting shape change of the above described supporting film material. And it is possible to use both non-crosslinked resin materials and resin materials with a low degree of crosslinking. In more details, for example, it is possible to use acrylic type resin material, urethane type resin material, polyester type resin material, vinyl chloride type resin material, vinyl acetate type resin material, polyolefin type resin material, fluorine containing type resin material, polyamide type resin material etc.. Each of these resins can be used individually or they can be used in as copolymer resins with other resin components, or as blends with other resin components. However, among those, the acrylic type resin material that has excellent weather resistance properties and has thermal melting properties that are easy to control, is especially appropriately used and preferred. And among those, acrylic resin materials, the acrylic type resin materials that have glass transition point in the range of  $-50 \sim 30^{\circ}\text{C}$  are especially preferably used.

[0023]

In the resin composition material that forms the structure of the supporting film material, besides the matrix resin material and the fibrous type material, depending on the requirements, it is also a good option to compound a coloring agent, a filler agent, an ultra-violet light absorbing agent, light stabilization agent, fluorescent light increasing white agent, properties improving agents etc..

[0024]

Also, depending on the requirements it is possible that a crosslinking (curing) agent is added and the supporting film material is thermally melted and its shape is changed and by that the continuous wall is formed and the transparent to the light protective film and the supporting film are partially connected. And after that the matrix resin material is crosslinked and the elongation strength, the impact resistance strength etc., of the support film material, are improved. However, in the case when an excess of a crosslinking agent is added, a deformation is generated based on the

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shrinking that is caused by the crosslinking reaction. And also, by the addition of that excessive crosslinking agent material, the elongation - contraction resistance strength of the supporting film material is decreased and because of that it is a good option if its used amount is limited as much as possible. And it is preferred to use a material where even when the amount of the used crosslinking agent is the largest, it is still in the range where the thermal plastification properties of the supporting film are not deteriorated.

[0025]

There are no specific limitations regarding the thickness of the supporting film that is used in the capsule type recurrent reflective sheeting material according to the present invention. However, usually, it is appropriate if the thickness is in the range of 20 ~ 150 microns.

[0026]

In order to provide even more excellent elongation - contraction properties to the supporting film material, it is also possible that on the back side of the supporting material film a reinforcing layer is formed that is formed from a crosslinked resin material etc.. Also, it is a good option if in the space between the above described supporting film material and the reinforcing layer an intermediate layer is provided with the goal to increase the adhesive strength between the former two layers, etc..

[0027]

In order to impart onto the capsule type recurrent reflective sheeting material according to the present invention still more excellent weather resistant properties, it is preferred that the elongation strength of the supporting film material at a temperature of 23°C is at least 50 kg/cm<sup>2</sup>, and that the extension to break is at least 50 %.

[0028]

Regarding the capsule type recurrent reflective sheeting material according to the present invention, it is a material that can be manufactured according to the already known from the previous technology materials and methods, with the exception of the fact that the supporting film material that is used is a material that is formed from a matrix resin material and fibrous shaped material. If we are to give one example, it would be according to the described here below paragraphs.

[0029]

Regarding the manufacturing of the capsule type recurrent reflective sheeting material, first, on a processed substrate material like a polyethylene terephthalate (PET) film, a solution of a resin composition material containing a matrix resin solution where a fibrous shaped material is homogeneously dispersed, is coated. Then it is dried and the supporting film material is obtained. On the other hand, on a temporary substrate material, like a paper laminate, laminated with polyethylene (PE), microscopic spherical lenses like glass beads are dispersed and coated, and by heating the diameter of the above described microscopic spherical lenses is buried densely as a single layer in the PE layer, to approximately  $1/5$  to  $1/3$  of the lense diameter. And after that on the surface of the exposed microscopic spherical lenses, aluminium etc., metal material is evaporated so that it covers the almost semi-spherical surface of the above described microscopic spherical lenses. By that a light reflective layer is formed and by that a lense type recurrent reflective elements are formed that are comprised of a large number of the microscopic spherical lenses. After that, on the top of these lense type recurrent reflective elements that are formed on the temporary substrate material, the surface of the supporting material film is contacted and placed over it. then by heating, the microscopic spherical lenses are buried into the supporting film up to approximately  $1/5$  to  $1/2$  of their diameter and the material is glued. After that, the temporary substrate material is removed and on the surface of the substrate material film the above described lense type recurrent reflective elements are transferred. After that, on the top of the protruding lense type recurrent reflective elements, a light transparent protective film, like an acrylic film, with a thickness in the range of 20 ~ 200 microns, is placed. And then, by using an embossing roll, and while heating the supporting film material, it is partially melted and the shape is changed, and the supporting film and the protective film are connected and by that a continuous wall is formed. However, by that a capsule lense type recurrent reflective sheeting is manufactured that contains a large number of capsules that contain a large number of lense type recurrent reflective elements.

[0030]

Regarding the manufacturing of the capsule cube - cone recurrent reflective sheeting material, the supporting film is formed the same way as in the above described paragraphs, and on the surface of the supporting film material, on the surface of one side, a light transparent protective film, that contains a large number of cube- cone type recurrent reflective elements, is placed so that the side with the cube- cone type recurrent reflective elements is facing that surface. By using an embossing roll etc., and while heating the supporting film material, it is partially melted and the shape is changed, and the supporting film and the protective film are connected and by that a continuous wall is formed. However, by that a capsule cube - cone recurrent reflective sheeting material is manufactured that contains a large number of

capsules that contain a large number of cube- cone type recurrent reflective elements.

[0031]

Depending on the desire, it is also a good option if on the capsule type recurrent reflective sheeting material according to the present invention, an adhesive layer is used, and in order to prevent the adhesion of dirt etc., on this adhesive agent layer, a release type substrate material etc., are formed on the back of the supporting film material, in that order

[0032]

#### [Practical Examples]

Here below, the present invention will be explained in more details by using practical examples and reference examples.

[0033]

#### Practical Example 1

Laminated processed paper where the paper is laminated with a PE material with a softening temperature of approximately 105°C, is heated to a temperature of approximately 105°C, and on the surface of that glass beads with an average particle diameter of approximately 65 microns and a refraction index of approximately 1.91, are homogeneously and also densely dispersed as a single layer. And after that, by using a nip roll at elevated pressure, the glass beads are buried in the PE to approximately 1/5 of their diameter. Next, on the exposed surface of the glass beads, aluminium is vacuum vapor deposited, and on the almost semi-spherical surface of the glass beads, a vapor deposited layer with a thickness of approximately 0.1 microns, is formed.

[0034]

After that, on the PET film with a thickness of 20 microns, and that has been subjected to a release treatment, a dispersion is coated. This dispersion is obtained by using as the matrix resin material, 167 weight parts of a 30 % solids acrylic type resin solution [methyl isobutyl (MIBK)/toluene solution of a material that is copolymerized from: ethylene acrylate (EA) - 53 weight %, methyl acrylate (MA) - 46 weight %, 2-hydroxy ethylmethacrylate (HEMA) - 1 weight %, acrylic acid (AA) - 0.1 weight %; and that has a weight average molecular weight of approximately 300,000; "Nissetsu KP-1684A, manufactured by Nippon Carbide Industries], and as the same matrix resin also 125 weight parts of a 40 % solids acrylic type resin solution [methyl

isobutyl (MIBK)/toluene solution of a material that is copolymerized from: ethylene acrylate (EA) - 66 weight %, methyl methacrylate (MMA) - 33 weight %, acrylic acid (AA) - 1 weight %; and that has a weight average molecular weight of approximately 250,000; "Nisetsu KP-1703A, manufactured by Nippon Carbide Industries]. Then as the fibrous type material, 10 weight parts of potassium titanate whiskers ["Tisumo - D, manufactured by Taicho Chemical Company), and then, 50 weight parts of rutile type titanium oxide and 30 weight parts of MIBK were stirred and mixed and this dispersion was used for the coating. A large part of the solvent was removed and the thickness of the layer on the supporting film material was approximately 80 microns.

[0035]

This supporting film material is placed over the prepared in advance processed paper with the buried glass beads that have been subjected to the vapor evaporation treatment, so that the supporting film and the glass beads are in contact. Then while heating at a temperature of 70°C, and at a line pressure of 900 kg/m, the glass beads are buried in the supporting film material to approximately 1/3 of the glass beads diameter, and the PE laminated paper is removed and the glass beads are transferred onto the supporting film material.

[0036]

After that, on the top of the supporting film material with the transferred glass beads, an unoriented acrylic film with a thickness of approximately 75 microns and a total light beam permeation coefficient of approximately 93 % [a multi-layer resin composition film, that contains a methyl methacrylate resin material as the matrix resin material and as a dispersed phase it has multilayer polymer crosslinked particles, formed mainly from MMA and butyl acrylate (BA) and with an average particle size of approximately 0.1 micron] is placed so that the glass beads and the acrylic film are in contact. After that a metal roll is used, whose surface is heated to a temperature of approximately 90°C and that has been subjected to a treatment whereby a network type protrusions have been formed, where the width of the lines in the network is approximately 0.3 microns. And also a rubber roll is used whose surface temperature is approximately 60°C. And the film is passed through the space between those two rolls, so that the acrylic film side is in contact with the rubber roll. And while it is passing through that gap, the metal roll is pressed from the side of the release treated PET film, and by that a partial thermal melting shape change is conducted.

[0037]



The release treated PET film is removed from the obtained thermally melted shape changed material, and on the side of the back surface of this support film material an approximately 40 microns thick acrylic type pressure sensitive agent ["Nissetsu KP-997", manufactured by Nippon carbide Industries], that has been formed separately on an approximately 75 microns thick silicone treated PET release type film, is glued as a laminate layer. By that, the recurrent reflective sheeting material is manufactured.

[0038]

The properties of the obtained recurrent reflective sheeting material are shown in Table 1. And in the case of the capsule type recurrent reflective sheeting material according to the present invention, even under severe weather resistance test conditions, the decrease of the reflective properties is small, and also the contraction is small, and then, there is almost no separation of the protective film. And because of that it is a material that has excellent weather resistance properties.

[0039]

#### Practical Example 2

Except for the fact that the fibrous type material that is added into the matrix resin composition material is changed to 10 weight parts of zinc oxide type fibrous shape material ["Panatetora", manufactured by Matsushita Amuteku Company], everything else was the same as described in the technological procedures according to the Practical Example 1. And by that the recurrent reflective sheeting material was manufactured. The properties of the obtained recurrent reflective sheeting material are shown in Table 1. And in the case of the capsule type recurrent reflective sheeting material according to the present invention, even under severe weather resistance test conditions, the decrease of the reflective properties is small, and also the contraction is small, and then, there is almost no separation of the protective film. And because of that it is a material that has excellent weather resistance properties.

[0040]

#### Reference Example 1

Except for the fact that the addition of the fibrous type material was eliminated, everything else was the same as described in the technological procedures according to the Practical Example 1. And by that the recurrent reflective sheeting material was manufactured. The properties of the obtained recurrent reflective sheeting material are shown in Table 1. And in this case under severe weather resistance test conditions, the decrease of the reflective

properties is large, and also the contraction is large. And the weather resistance properties are insufficient.

[0041]

Table 1

(Shown at the end of the translation.)

[0042]

Moreover, the tests that have been used according to the above described Practical Examples and reference Examples, are according to the shown here below.

[0043]

(1) Extension test of the supporting film

As the experimental specimen the material is cut to a width of 10 mm and a length of 50 mm and it is stored for 30 minutes at a temperature of 23°C. And after that, by using "Tensilon", manufactured by Polyentek Company, the extension measurements were conducted at a distance between the clasps of 10 mm, and at an extension rate of 200 mm/min. As the extensional strength the largest stress at that time was used and the extension obtained until the break point was taken as the extension to break value.

[0044]

(2) Test for weather resistance properties

The recurrent reflective sheeting material was cut to dimensions of 50 mm x 50 mm, and the silicone treated PET release film was separated and the recurrent reflective sheeting material was glued onto an aluminium panel. The glued experimental material was inserted into an accelerated weather resistance testing equipment ["light controlled weather meter, manufactured by Suga Measurement Equipment Company], and an accelerated weather resistance test was conducted for 500 hours.

[0045]

After that, the glued material is taken out and by using the cooling and heating cycle equipment [ "Heat Shock Chamber TSR-63", manufactured by Tabai Estek company] the heating and cooling cycle test was conducted. Moreover, regarding the cooling and heating cycle, one cycle is conducted

according to the described here below conditions, and 300 of these cycles were practically conducted.

[0046]

(Conditions for the cooling and heating cycle)

-40oC x 30 minutes -- room temperature x 15 minutes -- 145oC x 30 minutes --  
room temperature x 15 minutes

[0047]

(Measurement methods)

(2-1) Coefficient of decrease of the reflective properties

By using an equipment for the measurement of the recurrent reflective properties, manufactured by Advanced Retro Technology Company, "Model 920", the recurrent reflective properties of the experimental specimen after the weather resistance test, were measured. The recurrent reflective properties before and after the weather resistance test, were compared and the coefficient of the decrease of the recurrent reflective properties was calculated according to the described here below formula. Moreover, the conditions for the angles were, observation angle - 0.2o and incident angle 5o.

[0048]

[1]

Coefficient of decrease of the reflective properties =

$$= 1 - \frac{\text{recurrent reflective properties after the weather resistance test}}{\text{recurrent reflective properties before the weather resistance test}} \times 100$$

[0049]

(2-2) Contraction length (mm)

The contraction length of the protective film of the experimental specimen after conducting the weather resistance test was obtained as it is measured

from the edge at the largest contraction part, and based on this length<sup>1.8</sup> the contraction length is obtained.

[0050]

(2-3) Length of the separation of the protective film (mm)

The part where the connection between the protective film is separated from the supporting film in the experimental specimen after the conducting of the weather resistance test, is measured from the edge at the largest length break, and based on this length, this is made the length of the protective film separation.

[0051]

[Results from the present invention]

The present invention is an invention about a recurrent reflective sheeting, characterized by the fact that it is capsulated type recurrent refractive sheeting that is formed from at least a transparent to the light protective film, a supporting film and a continuous wall that is formed by thermal melting shape change from the above described supporting film; where the gap that remains in the space between the above described protective film and the supporting film is partially connected by the above described continuous wall, and recurrent reflection elements are densely positioned along the whole surface of the above described protective film and /or the supporting film; and in this recurrent reflection sheeting type, the above described supporting film contains a matrix resin and a fiber type material.

[0052]

By that, the supporting film material according to the present invention has excellent thermal melting shape change properties because it is easy to change the shape by thermal melting. And also at the time of the thermal melting shape change for the formation of the continuous wall, it is possible to achieve excellent adhesive strength in the space between the protective film and the continuous wall. And then, there is little deformation of the wall surface that forms the capsules and it has excellent elongation strength and resistant to repeated contraction, flexibility properties. And not only that but also this film has excellent outdoor long term resistance weather properties. And by that, it is possible to suggest a capsule type recurrent reflective sheeting material with excellent properties and where the problem points according to the previous technology have been solved.

Headings for table 1:

1. Example No., 2. Practical Example, 3. Reference Example, 4. parameter, 5. whiskers, 6. extension tests, 7. weather resistance tests, 8. name, 9. crystalline structure, 10. average fiber diameter (microns), 11. average fiber length (microns), 13. used amount (weight parts), 14. extensional strength (kg/cm<sup>2</sup>), 15. extension to break (%), 16. coefficient of the decrease of the reflective properties (%), 17. contraction length (mm), 18. protective film separation length (mm).

**Patent Assignee: Nippon Carbide Industries**

*Translated by Albena Blagev (6-7946)*

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\*【表1】

項目	ホ イ ス カ ー						引 張 試 験		耐 候 性 試 験		
	品 名	結 晶 構 造	平 均 繊維径 ( $\mu\text{m}$ )	平 均 繊維長 ( $\mu\text{m}$ )	平 均 7 $\times$ 10 $^4$ 外 比	使用量 (重量部)	引張強度 ( $\text{kg}/\text{cm}^2$ )	破断伸び (%)	反射性能 低下率 (%)	収縮長さ (mm)	保護フィルム 剥がれ長さ (mm)
実施例 1	ポリエステル D	針 状	0.5	15	30	10 <sup>13</sup>	150	200	0	1	0
実施例 2	ポリエステル	針状	1.0	25	25	◇	175	185	◇	0	◇
比較例 1	—	—	—	—	—	—	43	420	15	4	15